PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AFB/JAS/P8870WO	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/IB 03/00695	International filing date *(day/month/year)* 24.02.2003	Priority date *(day/month/year)* 25.02.2002
International Patent Classification (IPC) or both national classification and IPC C01B3/38, C01B3/38		
Applicant AIR PRODUCTS AND CHEMICALS INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24.09.2003	15.06.2004
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IB 03/00695

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-24	as originally filed

Claims, Numbers

1-28, 29 (part)	as originally filed
29 (part), 30-42	received on 16.04.2004 with letter of 16.04.2004

Drawings, Sheets

1/3-3/3	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☒ the claims, Nos.: 43

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2, 4-7, 9, 10, 12-17, 19, 21-31, 34, 35, 38-42
	No:	Claims	1, 3, 8, 11, 18, 20, 32, 33, 36, 37
Inventive step (IS)	Yes:	Claims	29-30, 39-41
	No:	Claims	1-28, 31-38, 42
Industrial applicability (IA)	Yes:	Claims	1-42
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: DE-A-4340688 (Uhde GmbH)
D2: WO-A-94/26656 (Gastec NV)
D3: GB-A-2168718 (Humphreys & Glasgow Ltd.)

1. Claims 1, 29, 31, 32, 39 and 42 do not fulfil the requirements of Article 6 PCT.

1.1. The present application does not fulfil the requirements of Article 6 PCT, because the claims 1, 29, 32 and 39 are not supported by the description.

The claims are in its broadest sense directed to a process and an apparatus in which the product of a partial oxidation is cooled by introduction of a reactive diluent fluid which is reacted in a second reactor. This term "reactive diluent fluid" comprises an extremely large number of possibilities, whereas in the application only support can be found for carbon dioxide, water, hydrocarbons and molecular hydrogen.

Furthermore, the passage "reacting said reactive mixture in a second reactor to produce a reacted syngas product" also does not seem to be supported by the description. The application only seems to provide support for the reverse water gas shift reaction and for the gasification of solid carbon particles as specified in claims 29 and 39. No other such reactions have been disclosed in the application as filed.

It would therefore appear that a main claim should be based on a combination of claims 1 and 29, in which the "reactive diluent fluid" is further defined as indicated above.

In his reply to the written opinion, the applicant has argued that claims 1, 29, 32 and 39 are supported by the description. Reference in this respect was made to page 9, line 22 - page 10, line 6; page 15, line 23 - page 16, line 6; page 16, line 20 - page 17, line 5 and page 17, line 32 - page 18, line 22. In these passages, the wording of the claims can indeed be found. However, the presence of the

wording of claim in the description does not necessarily mean that a claim is supported by the description. The claims are supported if the person skilled in the art would be able, on the basis of the information given in the application as filed, to extend the particular teaching of the description to the whole of the field claimed by using routine methods of experimentation or analysis. In his reply to the written opinion the applicant has alleged that this is the case here. The examiner cannot agree on this point of view, because neither the reaction ("reacting [...] to produce a reacted syngas product"), nor the reactant ("reactive diluent fluid") are defined in the claims. A large number of liquid and gaseous organic and inorganic compounds will be able to react with the synthesis gas and therefore qualify for the term "reactive diluent fluid".

Claims 1, 29, 32 and 39 are not supported by the description.

A main claim based on a combination of claims 1 and 29, in which the "reactive diluent fluid" is further defined as indicated above, would have been supported by the description.

1.2. Claims 31 and 42 do not fulfil the requirements of Article 6 PCT in combination with Rule 6.2 PCT which defines that claims shall not, except where absolutely necessary, rely on references to the description or drawings. In the present case, a reference to the drawings is not considered absolutely necessary.

2. The present application does not satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of claims 1, 3, 8, 11, 18, 20, 32, 33, 36 and 37 is not new in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

2.1. Document D1 discloses a process and apparatus for the production of synthesis gas. In an exothermal zone, a hydrocarbon is partially oxidised. The hot product gases of this partial oxidation serve to heat an endothermic reforming reaction, by passing the hot gases on the outside of the catalytic tubes. Before the hot gases are passed to heat the endothermic reaction, water is injected to cool the gases in order to avoid metal dusting corrosion (see figures 1, 2; page 3, lines 2-47).

The gases into which the steam is injected are extremely reactive gases and some reaction with the steam will therefore take place. The area in the reactor 2 where the steam is injected can, therefore, certainly be considered as second reactor as defined in claims 1 and 32.

The applicant has argued in his reply to the written opinion that there is no explicit disclosure of reaction with water in D1. The examiner agrees with the applicant on this point.

The applicant has further argued that reaction with water is also not an inevitable result of the D1 process. The examiner cannot agree on this point of view expressed by the applicant. In D1 a hot synthesis gas is contacted with water on the shell side of a heat exchange reformer. Of course, at least some reaction will take place between the synthesis gas (above 1200°C, see D1: page 3, line 4) and the water. It is not in this respect that the **claims do not define any level conversion**, so even a low conversion fall under the claims.

The subject-matter of claims 1, 3, 8, 18, 20, 32, 33, 36 and 37 is not novel.

2.2. Document D2 discloses a process for producing synthesis gas in which an exothermic catalytic partial oxidation is followed by an endothermic steam reforming. Carbon dioxide, steam or methane is added between the two reaction steps (see page 9, lines 9 - page 10, line 11).

As for document D1, the injection of carbon dioxide, methane or steam in a very reactive stream, will lead to reaction.

With respect to D2, the applicant has provided, in his reply to the written opinion, very similar arguments as for D1, ie that it would not be implicitly disclosed in D2 that reaction takes place between the exothermically generated gas and the steam and/or methane and/or carbon dioxide.

As for D1, the examiner maintains that also in D2 at least some reaction will take place between the exothermically generated gas and the steam and/or methane and/or carbon dioxide.

The subject-matter of claims 1, 3, 8, 11, 18 and 32 is not novel.

3. It is not apparent how the subject-matter of claims 2, 4-7, 9, 10, 12-17, 19, 21-28, 31, 34, 35, 38 and 42 could form the basis for a main claim which is novel and involves an inventive step.

It would appear to the examiner that most features of those claims are known

features to the person skilled in the art of reforming.

4. The subject-matter of, what can be understood of claim 29, is novel and inventive over the prior art cited in the search report.

   Document D3 discloses a process for producing synthesis gas in which a hydrocarbon is either reformed or partially oxidised. To cool the gases, carbon dioxide is added so that the reverse water gas shift reaction takes place (see whole document).

   The difference between claim 29 and document D3 lies in the fact that in claim 29 an additional step of gasifying solid carbon particles in the mixture takes place.

   There is no indication in the prior art to let this reverse water gas shift reaction be followed by a gasification of solid carbon particles.

   The subject-matter of claim 29 is novel and involves an inventive step.

   Similar comments are valid for claim 39.

5. The subject-matter of claims 31, 40 and 41 are also novel and involve an inventive step, because these claims concern preferred embodiments of claims 29 and 39, respectively.

exothermically reacting hydrocarbon-containing fuel with an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product;

cooling an effluent stream of said exothermically-generated syngas product by combining reactive diluent fluid with said stream to produce a mixture comprising cooled exothermically-generated syngas product and reactive diluent fluid, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;

said process further comprising:

reacting together carbon dioxide in said mixture with molecular hydrogen in said mixture over a catalyst in a second reactor to produce reacted syngas product that is enriched in carbon monoxide; and

gasifying solid carbon particles in said mixture with at least one other component in said mixture in a second reactor to produce reacted syngas product that is depleted in solid carbon.

30. A process as claimed in Claim 29 further comprising endothermically reforming hydrocarbon-containing fuel gas with steam over a catalyst in a heat exchange reformer to produce heat exchange-reformed syngas product wherein at least a portion of the heat generated in the exothermic reaction producing said first syngas product is used to drive the endothermic reforming reaction.

31. A process substantially as hereinbefore described with reference to the accompanying figures.

32. Apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen according the process defined in Claim 1, said apparatus comprising:

a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;

conduit means for removing an effluent stream of said exothermically-generated syngas product from the first reactor;

means for combining a stream of reactive diluent fluid with said effluent stream to produce a reactive mixture;

a second reactor in which said reactive mixture reacts to produce a reacted syngas product;

a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a heat exchange-reformed syngas product; and

conduit means for feeding a stream of reacted syngas product from the second reactor to the heat exchange reformer;

wherein at least a portion of the heat required in the generation of said heat exchange reformed syngas product is obtained by recovering heat from said reacted syngas product thereby cooling said reacted syngas product.

33. Apparatus as claimed in Claim 32 wherein the first reactor is selected from the group consisting of a partial oxidation ("POX") reactor, an autothermal reformer ("ATR") and a catalytic partial oxidation ("CPO") reactor.

34. Apparatus as claimed in Claim 32 or Claim 33 wherein the reactive mixture comprises carbon dioxide and the second reactor has a reverse water gas shift reaction zone in which at least a portion of the carbon dioxide and at least portion of the molecular hydrogen in said mixture are reacted together over a catalyst to produce a carbon monoxide-enriched syngas product.

35. Apparatus as claimed in any of Claims 32 to 34 wherein the reactive mixture comprises solid carbon particles and the second reactor has a gasification reaction zone in which at least a portion of the solid carbon particles is gasified by reaction with at least one other component of the mixture to produce a solid carbon-depleted syngas product.

36. Apparatus as claimed in any of Claims 32 to 35 wherein the heat exchange reformer is a shell and tube style reformer in which the endothermic reforming reaction occurs within the tubes and the reacted syngas product is introduced to the shell-side.

37. Apparatus as claimed in any of Claims 32 to 36 wherein the reformer is an enhanced heat transfer reformer ("EHTR").

38. Apparatus as claimed in any of Claims 32 to 37 further comprising means for combining a second diluent fluid with a syngas stream between the point at which the reactive diluent is combined with said exothermically-generated syngas product and the point at which heat is recovered from the reacted syngas product to adjust the temperature and/or change the composition of relevant syngas stream.

39. Apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen according to the process defined in Claim 29, said apparatus comprising:

a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;

a second reactor;

conduit means for feeding an effluent stream of said exothermically generated syngas product from the first reactor to the second reactor;

means for combining reactive diluent gas with said effluent stream to produce a mixture comprising cooled exothermically-generated syngas product and reactive diluent gas, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;

said apparatus further comprising:

a reverse water gas shift reaction zone in which carbon dioxide in said mixture is reacted together with molecular hydrogen in said mixture

over a catalyst in the second reactor to produce a reacted syngas product that is enriched in carbon monoxide; and

a gasification reaction zone in which solid carbon particles in said mixture are gasified with at least one other component in said mixture in the second reactor to produce a reacted syngas product that is depleted in solid carbon.

40. Apparatus as claimed in Claim 39 further comprising:

a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a heat exchange reformed syngas product;

conduit means for feeding reacted syngas product from the second reactor to the heat exchange reformer;

wherein at least a portion of the heat generated in the exothermic reaction producing said exothermically generated syngas product is used to drive the endothermic reforming reaction.

41. Apparatus as claimed in any of Claims 32 to 40 wherein the first reactor is a partial oxidation ("POX") reactor and the reformer is an EHTR.

42. Apparatus substantially as herein before described with reference to the accompanying figures.